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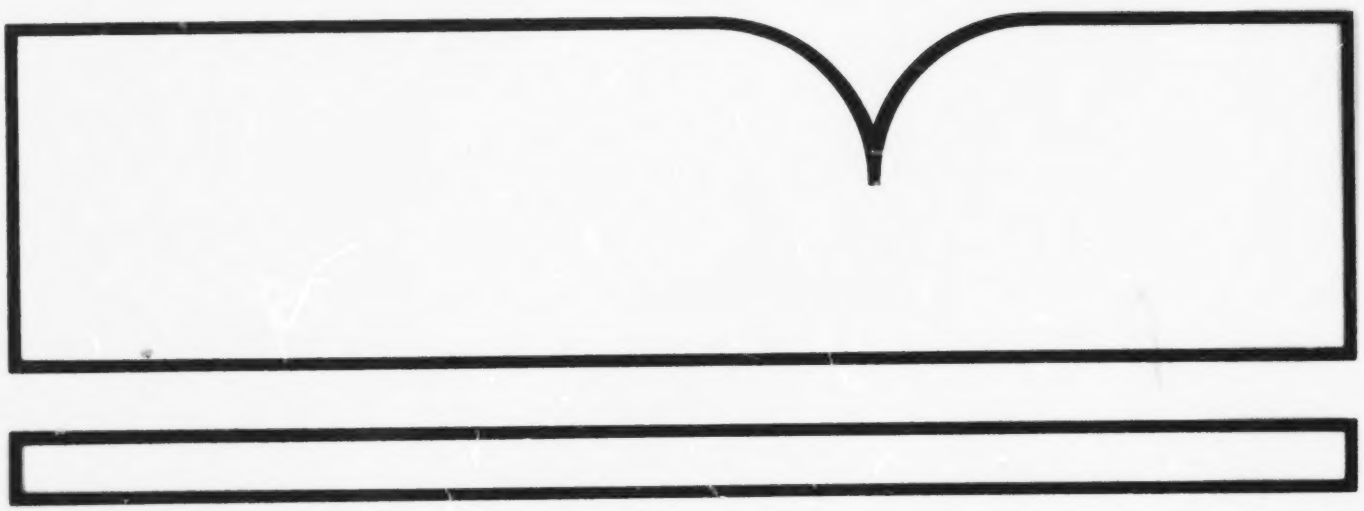

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16. ABSTRACT

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9 Hydrolytic Transformations of Organic Chemicals in the Environment

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Large quantities of pesticides are introduced into the environment for a variety of uses. Pesticides enter environmental compartments as a result of direct application, spray drift, or disposal. The parent chemicals and their degradation products can enter the aquatic environment by runoff into surface waters, by leaching into groundwaters, and by erosion of contaminated soils into streams (Sharom et al., 1980). The environmental fate of these pollutants depends to a considerable extent on the interactions between the pesticides and the solid surface of soil or sediment systems. These interactions influence the efficiency of pesticides and their ultimate fate in the environment.

The environmental factors that effect the persistence of these biologically active synthetic chemicals in the environment are only now becoming fully apparent (Mabey & Mill, 1978). Fortunately from the environmental perspective, transformation processes including hydrolysis, oxidation-reduction, and photodegradation lead to the decomposition of these pollutants. The rate at which these chemicals undergo transformation depends on the physical and chemical properties of each compound and in fact varies greatly from compound to compound.

Hydrolysis is a significant process in determining the fate of many pesticides. For many compounds, hydrolysis can be the dominant pathway for their transformation in the environment (Mabey & Mill, 1978). Often hydrolysis of selected functional groups is required before microbial degradation can be initiated. Some organic functional groups, however, are relatively or completely inert with respect to hydrolysis under reaction conditions that

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exist in most ecosystems. Functional groups that are potentially susceptible to hydrolysis are shown below (Mabey & Mill, 1978):

1. Amides.
2. Carbamates.
3. Epoxides.
4. Aliphatic and aromatic esters.
5. Alkyl and aryl halides.
6. Nitriles.
7. Phosphorus esters.
   a. Phosphonates.
   b. Phosphates and thiophosphates.
   c. Phosphonohalidates.

In the environment, hydrolysis reactions can be biologically mediated or occur via abiotic processes. For biotic hydrolysis reactions, the rate of hydrolysis is often proportional to bacterial biomass and/or specific enzyme concentration (activities) in the medium. In abiotic hydrolysis reactions, the hydrolysis rates can be a function of chemical parameters such as H ion activity (pH), dissolved organic matter, and dissolved metal ions. For many compounds, both abiotic and biotic hydrolytic processes contribute to the disappearance of pollutants in the environment. The focus of this chapter is on factors that influence the rate of abiotic hydrolysis reactions in soils and sediments.

9-1 WATER

In general, hydrolysis is a bond-making bond-breaking process in which a molecule, RX, reacts with water forming a new C-O bond and cleaving a carbon-X bond in the original molecule. One possible pathway is by a direct displacement of X with HO^- as shown in Eq. [1] (Aly & El-Dib, 1971):

$$RX + HO^- \xrightarrow{H_2O} ROH + X^-. \qquad [1]$$

The detailed mechanisms of hydrolytic processes are well defined and have been shown to involve the formation of intermediates such as protonated species, anionic and carbonium ions, as well as combinations of these intermediates.

9-1.1 Kinetics

In general, hydrolysis of organic chemicals in water under pH-buffered conditions is first-order in the concentration of the organic species (RX) where the rate of the hydrolysis ($d[RX]/dt$) is proportional to the concentration of pollutant RX:

$$d[RX]/dt = -k_{obs}\,[RX]. \qquad [2]$$

where k_{obs} is the observed pseudo-first-order disappearance rate constant. The first-order dependence of the disappearance rate on the [RX] is important, because it implies that the half-life ($t_{1/2}$) of the reaction (Eq. [2]) is independent of [RX]. Thus, the results obtained at a high RX concentrations can be extrapolated to lower RX concentrations if the reaction conditions are held constant. The half-life of the reacting compound is given in Eq. [3]:

$$t_{1/2} = \ln(2)/k_{obs}. \qquad [3]$$

where k_{obs} can include contributions from acid- or base-catalyzed hydrolysis, nucleophilic attack by water, or catalysis by buffers in the reaction medium. Hydrolysis half-lives conveniently put in perspective the susceptibility of pesticides to hydrolysis (Burkhard & Guth, 1981).

For abiotic hydrolysis, the general expression for k_{obs} is given below:

$$k_{obs} = k_H[H^+] + k_{OH}[OH^-] + k_w + \sum_i (k_{HA}[HA] + k_A[A^-]). \qquad [4]$$

where k_H and k_{OH} are the specific acid-base catalyzed second-order rate constants, respectively; k_w is the neutral hydrolysis rate constant; and k_{HA} and k_A are the general acid-base catalyzed hydrolysis rate constants, respectively. In Eq. [4], $[H^+]$ and $[OH^-]$ are the hydrogen and hydroxyl ion concentrations (activities), respectively, and [HA], $[A^-]$ are the concentrations (activities) of the ith pair of general acids and bases in the reaction mixture.

Unfortunately, for most environmental studies disappearance rate constants are measured in such a way that it is not possible to distinguish between abiotic and biotic contributions. One readily distinguishing factor, however, is a lag period. For example, biotic hydrolysis is often but not always characterized by an initial lag period during which little or no change in concentration occurs. This is followed by a more rapid change in concentration where its natural log is generally linear with time. In laboratory studies, several pesticides including dalapon (2,2-dichloropropionic acid), chloridazon [5-amino-4-chloro-2-phenyl-3-(2*H*)-pyridazinone], and 2,4-D [(2,4-dichlorophenoxy) acetic acid] have been shown to exhibit this kind of kinetics (Hurle & Walker, 1980). On the other hand, abiotic hydrolysis under buffered pH conditions, unless an auto catalytic reaction takes place, does not exhibit such a lag phase.

Many halogenated hydrocarbons including pesticides have been found to be resistant to microbial transformation (Armstrong et al., 1967; Harris, 1967; Haag et al., 1986). It appears that the first step in the degradation of these compounds is abiotic hydrolysis. The rate of hydrolysis is proportional to the pesticide concentration and the results can often be modeled using first-order kinetics. As Eq. [4] implies, the following parameters contribute to the rate of hydrolysis.

9-1.2 Role of pH

The rate of hydrolysis of an organic compound can be affected by pH, either by specific acid-base effects or by a change in compound speciation. The most common is specific acid or base-mediated hydrolysis (the first two terms in Eq. [4]) where the rate of reaction is directly proportional to the hydrogen or the hydroxyl-ion activity (Harris, 1982). The second effect is the result of shifting the equilibrium of ionizable compounds that contain acidic or basic functional groups. A small change in pH can shift the equilibrium in favor of the charged or uncharged species, which often have different reaction rate constants (Harris,1982).

The predominant (Eq. [4]) hydrolysis pathways in natural waters are usually acid-catalyzed, base-mediated, and neutral (pH-independent) hydrolysis. Acid-catalyzed hydrolysis reaction rates increase with decreasing pH and the rate is directly proportional to the hydrogen ion activity. Base-mediated hydrolysis reaction rates increase with increasing pH and the rate is directly proportional to the hydroxyl ion activity. For neutral hydrolysis reactions, the rates are independent of pH, thus the contribution of the first two terms in Eq. [4] to the overall hydrolysis will depend on the magnitudes of the rate constants and the pH.

The effect of pH on the rates and the mechanisms of hydrolysis reactions of pesticides in well-defined systems such as buffer solutions and natural water samples has been studied under a variety of laboratory conditions. For example, Macalady and Wolfe (1983) demonstrated in detail that organophosphorothioate esters (such as chlorpyrifos) undergo neutral and alkaline hydrolysis in natural and buffered water samples. The disappearance hydrolysis rate constants for these esters are pH independent over the range of 1 to 7 pH. Above pH 8, alkaline hydrolysis dominates but the first-order rate constants were not directly proportional to the hydroxyl ion activity. Predominantly, hydrolysis occurred as a result of the cleavage of the P-O bond at alkaline pHs and via cleavage of the methyl C-O bond at neutral and acidic pHs, accompanied with formation of the corresponding acid and alcohol. Alkaline-mediated hydrolysis reactions were also observed for fenitrothion as shown in Fig. 9-1 (Greenhalph et al., 1980); iprodione (Belafdal et al., 1986); Zectran (Matthews & Faust, 1977); and DDT (Wolfe et al., 1977).

Acid-catalyzed and neutral hydrolysis pathways were observed in the hydrolysis of chlorostilbene oxide (CSO) in pH-buffered distilled water as well as natural water samples (Metwally & Wolfe, 1989). Acid-catalyzed hydrolysis dominated below pH 5; at higher pHs, only neutral hydrolysis contributed to the disappearance of CSO (Fig. 9-2).

The studies of Armstrong et al. (1967), Li and Felbeck (1972), and more recently by Plust et al. (1981) indicated that atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5 triazine) undergoes acid and base catalysis at extreme acidic and basic pHs in aqueous systems. Extrapolation of the above data predicts that a minimum in the pH-rate profile occurs at pH 7. These find-

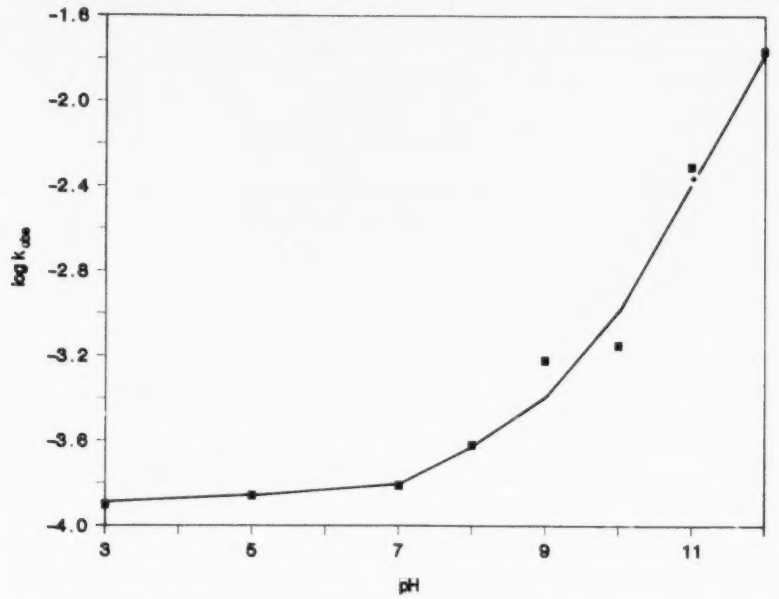


Fig. 9-1. Plot of pH vs. observed rate constant for the hydrolysis of fenitrothion (10 ppm) at 49.7 °C and in dark.

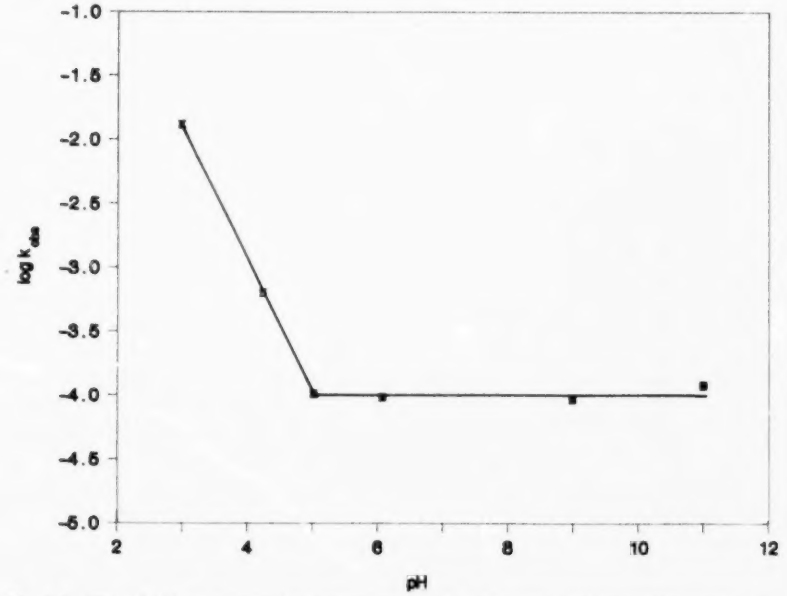


Fig. 9-2. Plot of pH vs. observed rate constant for the hydrolysis of chlorostilbene oxide in 1 m*M*-buffered water and at 25 °C.

ings are consistent with the findings of Metwally and Wolfe (1988, manuscript in preparation).

9-1.3 Effect of Temperature

Temperature effects can be pronounced on the rate of hydrolysis of pesticides in aqueous ecosystems. The relationship between temperature and the rate constant of the reaction is commonly expressed by the Arrhenius equation:

$$k_{obs} = Ae^{-E_a/RT} \quad [5]$$

where A is the collision frequency, E_a (kcal/mol) is the activation energy, R is the universal gas constant, and T ($K°$) is the reaction temperature (Harris, 1982). For a compound with an activation energy of 17 to 18 kcal/mol, an increase in temperature of 1 °C will cause a 10% increase in the rate constant, and a 10 °C increase in temperature will increase the rate constant a factor of 2.5 (Harris, 1982).

9-1.4 Dissolved Metal Catalysis

Acceleration of the rate of hydrolysis of pesticides, relative to distilled water at a given pH, by soluble metals has been the subject of recent investigations. Blanchet and St.-George (1982) found in laboratory studies that the rate of the hydrolysis of chlorpyrifos-methyl increased with increasing Cu^{2+} concentration. Metal ions such as Ca, Mg, Fe, Co, and Ni were shown to catalyze the hydrolysis of organophosphorus pesticides (Meikle & Youngson, 1978). Extrapolation of the results to metal ion concentrations that exist in natural waters suggests, however, that soluble metal ions will not play a significant role in the hydrolysis of organic compounds under reaction conditions common to most natural waters. Additional research in metal catalysis is necessary to support this hypothesis.

9-1.5 Buffer Catalysis

Based on Eq. [4], buffers present in the reaction medium can contribute to the hydrolytic processes. Buffer catalysis will be more significant for pH independent reactions. Organic and inorganic acids along with their conjugated bases are usually common in natural waters and exhibit a wide variation in structure and concentration. Because of this, a general approach is needed to assess their contribution to hydrolysis. Perdue and Wolfe (1983) showed that by using a mathematical approach, the maximum-predicted buffer-catalysis contribution will be $< 10\%$ of the uncatalyzed process.

9-1.6 Effect of Dissolved Humic Materials

Several investigators have suggested that dissolved humics affect the environmental fate of pesticides in natural waters. Humic materials have been

shown to increase the solubility of certain hydrophobic pesticides such as DDT and affect the kinetics of reaction in water (Carter & Suffet, 1982). Struif et al. (1975) observed an enhancement in the hydrolysis rate constants of 2,4-D esters by dissolved organic materials in aqueous solutions. Perdue and Wolfe (1982) measured the rate of alkaline hydrolysis of the octyl ester of 2,4-D in the presence and absence of soluble humic materials in water. They found that the second-order rate constant for hydrolysis in the presence of humic material was lower than in distilled water. They suggested that the fraction of 2,4-D ester partitioned to the humic material did not undergo alkaline hydrolysis. They attributed the increase in the rate of hydrolysis of 2,4-D esters observed by Struif et al. (1975) to microbially mediated hydrolysis.

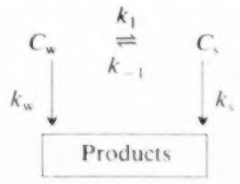
9-2 SEDIMENTS

9-2.1 Partitioning

Sediments constitute an important sink and/or source for aquatic pesticides and other organic chemicals. The ability of river and lake sediments to sorb and affect the hydrolysis of organophosphorus compounds was investigated by Rodel et al. (1977). They monitored the concentration of two organic compounds, inositol hexaphosphate and glycerophosphate, in sediment-water systems in both the aqueous and solid phases. They found that the distribution among compartments changed with time as sorption and hydrolysis occurred. They concluded that sorption to the sediment strongly inhibited the hydrolysis of the compounds and suggested that the reaction was retarded because the compound in the sorbed phase was not accessible by the enzymes in the system.

9-2.2 Heterolytic Kinetics

In the case of abiotic hydrolyses, it was recently shown for selected organic compounds, that hydrolysis can occur in the sediment sorbed phase depending on the compound and the reaction mechanism (Wolfe et al., 1977, 1979). Recently, Macalady and Wolfe (1985) determined the kinetics of hydrolysis of three organophosphorothioate pesticides in selected sediment-water samples to define the role of hydrolysis in the sediment-sorbed phase. The authors proposed the following model to represent the kinetics of hydrolysis of the pesticides in sediment/water systems (Eq. [6]).



[6]

where C_w and C_s are the concentrations of the pesticide in the aqueous and sediment phases, respectively; k_1 is the pseudo-first-order constant for the sorption process; k_{-1} is the first-order rate constant for desorption; k_w is the first-order rate constant for the hydrolysis of the pesticide in the aqueous phases; k_s is the rate constant for the pesticide in the sorbed phase.

9-2.3 Reactions of Organic Compounds

Depending on the reaction, the hydrolysis of several pesticides in sediment samples appears to be consistent with the above model. Maclady and Wolfe (1984) studied the abiotic hydrolysis of several sorbed pesticides in different sediment-water systems and found that, in the solid sorbed phase, base-mediated rate constants were substantially retarded, the acid catalyzed rate constants were enhanced. Neutral hydrolysis rate constants, however, were similar when referenced to the rate constants in the aqueous phase.

In similar studies, Haag et al. (1986) reported that the presence of low-carbon sediment solids had no effect on the hydrolysis of halo-alkenes and alkanes such as isopropyl bromide, 1,1,1-trichloroethene, and 1,1,2,2-tetrachloroethene. Therefore, kinetic and product data obtained in pure water or any other homogeneous system would be applicable to sediment-water systems.

Recently, Wolfe (1987, unpublished data) found that, in aquifer materials with low organic C, that there was no detectable heterogeneous catalysis by

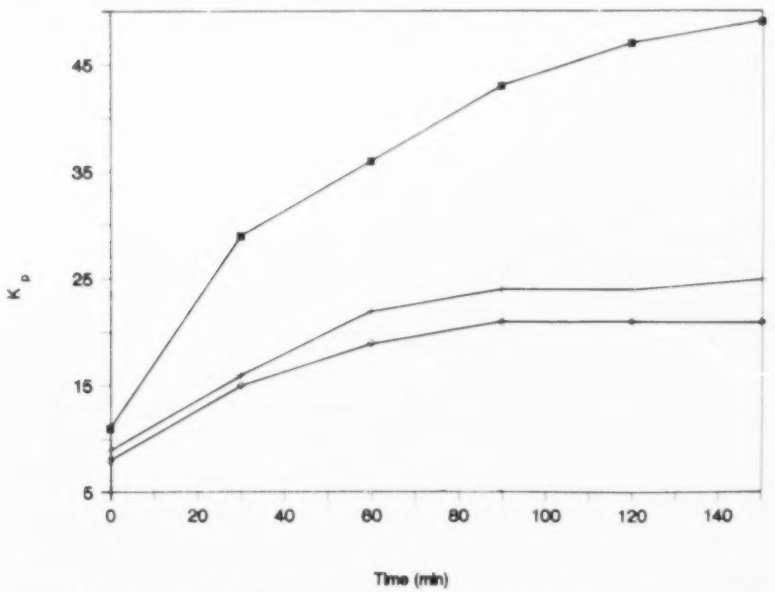


Fig. 9-3. The effect of time on the adsorption of 1,4-DCB on aquifer samples collected from Oregon (squares), Florida (crosses), and Wisconsin (diamonds).

the solid particles. Also, Moftah and Wolfe (1988, unpublished data) found that the major effect of solid particles was that of partitioning. These authors, also, observed the importance of organic C in the adsorption process of the chemicals on the sediment phase. In their studies on the abiotic transformation of 1,4-dichloro-2-butene (1,4-DCB) in aquifer material, they found that K_p correlated with the organic C content of the aquifer material ($r^2 = 0.95$): In addition, they also observed that K_p increased with time (Fig. 9–3) until reaching a constant value after about 140 min.

The ability of clay minerals to catalyze the hydrolysis and rearrangement reactions of alkenes (Balantine et al., 1983) and other organic compounds (Cornijo et al., 1983) is well known. The mechanisms of the catalytic processes have been the subject of considerable speculation. In this respect, Cornijo et al. (1983) and Singhal and Singh (1976) stated that the clay mineral smectite can be important in the degradation of organic compounds due mainly to its expendability and high surface area and to the fact it contains electrolytes such as H^+, Na^+, or Ca^{2+}. The study of Camazano and Martin (1983) indicated that the degradation of the pesticide, phosmet, was 500-fold greater in the presence of 2:1 type clay montmorillonite than in a clay-free system because the clay-chemical interaction enhanced the electrophilic nature of the organophosphorothioate molecule, thus facilitating its nucleophilic attack by the OH^- ions.

9-3 SOILS

Knowledge of degradation rates and transformation of pesticides in soils is important to agricultural practice and environmental safety. Because soil is a complex biological and chemical medium, the kinetics of hydrolysis are less straight forward than in natural waters. It is expected that sorption of the pesticide by the solid particles will affect the kinetics of hydrolysis. Also because of enhanced microbiological activity in soil, it becomes more difficult to separate the abiotic and biotic processes. Moreover, there may be competing reaction sequences within the hydrolysis process (Hurle & Walker, 1980). Therefore, it is not surprising that deviations from simple first-order reaction kinetics are observed. These deviations could well be influenced by several factors as discussed below.

9-3.1 Soil Type

Recent studies by Moftah and Wolfe (1988, unpublished data) on the hydrolysis of 1,4-DCB (Table 9–1) and Sharom et al. (1980) on the hydrolysis of several other pesticides, showed that the proportion of sand/silt/clay plays a significant role in the hydrolysis of organic compounds. The greater the fraction of clay, the greater the hydrolysis rates. A clay mineral with a ratio of 2:1 has a greater effect on the hydrolysis than a clay mineral with a 1:1 ratio. Presumably, 2:1 clay has a greater surface area and higher CEC. Depending on the exchange capacity and type of clay, certain metal ions can

Table 9-1. The effect of physical and chemical properties of sediment and hydrolysis of 1,4-DCB.

	AR†	FL	OK	OR	WI
Texture:					
Sand, %	96.20	90.44	73.91	40.58	99.26
Silt, %	0.66	2.01	23.09	26.99	0.58
Clay, %	3.14	7.55	3.00	32.43	0.16
Organic matter, %	0.021	0.234	0.011	0.870	0.107
CEC [$cmol_c\ kg^{-1}$]	3.40	12.88	1.84	28.71	6.84
$k_{obs} \times 10^{-4}$	18.00	33.50	16.50	45.34	27.26

† AR = Sediment collected from Arkansas.
FL = Sediment collected from Florida.
OK = Sediment collected from Oklahoma.
OR = Sediment collected from Oregon.
WI = Sediment collected from Wisconsin.

catalyze the hydrolysis of selected organic compounds. Early studies by Bender (1963) and Epstein and Mosher (1968) showed that certain species of metals such as Cu^{2+}, Zn^{2+}, Mn^{2+}, Al^{3+}, and Fe^{3+} were effective in accelerating the hydrolysis of selected organic compounds. A mechanism to account for the accelerated hydrolyses by metal ions was proposed by Buckingham and Engelhardt (1975). They suggested that the metals increase the hydroxide ion activity at the solid surface relative to the bulk aqueous pH.

9-3.2 Organic Carbon

Organic C has been shown to be an important sorbent for pesticides in soils and has been suggested to have an effect on biological and nonbiological degradation processes. Studies by Hance (1974) showed that hydrolysis of atrazine was decreased significantly in sterilized soil samples when the organic C was removed. On the other hand, sorption of hydrophobic pesticides increases with increasing organic C but because sorption decreases the amount of the compound in aqueous solution, it might be expected to inhibit degradation. For instance, 2,4-D was hydrolyzed more rapidly in soils with higher organic C content; in contrast Harris et al. (1969) observed a negative correlation between the rate of hydrolysis of several pesticides and soil organic C content. For these reasons, Hamaker (1972) suggested that an increase in organic C might increase rates of chemical degradation in mineral soils up to a limiting value above which the rate of loss would be retarded. Recently, Chapman and Cole (1982) reported that hydrolysis of landrin, a carbamate pesticide, was greater when the organic C was in the range of 0.1 to 0.8%. The pesticide was degraded much more slowly in soils with organic C contents of 1 to 1.9%, suggesting that the organic C may mask the acidity or alkalinity of the soil with respect to chemical hydrolysis.

9-3.3 Adsorption of Pesticides

The effect of sorption on hydrolysis rates has been studied by many investigators and conflicting conclusions have been reported. In a study by

Mayer et al. (1972), the increase in sorption of atrazine and chlorthiamid decreased the hydrolysis rate and increased the persistence of the compound in soil. In contrast, Armstrong et al. (1967), Russell et al. (1968), and Lightfoot et al. (1987) reported faster degradation of adsorbed atrazine, aldicarb, aldicarb sulfoxide, and aldicarb sulfone in sterile soil than in aqueous solution. They suggested that enhanced hydrolysis was a result of surface-catalysis.

Russell et al. (1968) described the sorption-catalyzed abiotic hydrolysis of triazine pesticides in soils as follows: sorption results from H-bonding between the carboxyl groups on the soil particles and the N atom of the triazine ring, that leads to protonation of the ring or side-chain N atom, this activates the C-Cl bond and results in cleavage of the C-Cl bond by water.

9-3.4 Soil pH

The soil pH can be expected to influence the hydrolysis of pesticides either directly if the hydrolysis is pH dependent or indirectly via the effect of sorption of the chemical on the soil particles. In contrast, in a study using sterilized soils, Chapman and Cole (1982) reported no correlation between the measured pH and soil type and the rate of disappearance of organochlorine, organophosphorus, carbamate, and pyrethoid pesticides. Similarly, a lack of a correlation between soil pH and disappearance rate of 1,4-DCB also was observed by Moftah and Wolfe (1988, unpublished data).

The above findings demonstrate the difficulty of extrapolating the pH dependent disappearance behavior observed in homogenous systems to heterogenous systems such as soil.

9-3.5 Soil Temperature

Because soil surfaces can reach high temperatures in the summer sunlight, it is necessary to be able to predict hydrolysis rate constants at elevated temperatures. For most abiotic hydrolysis reactions, hydrolysis rate constants generally increase with increasing temperature. Although the effect of temperature on rate constants can be described by several different expressions, the most widely used is the Arrhenius equation as given above (Eq. [5]). Difficulty in using such a relationship for predicting the disappearance of pesticides and other organic compounds in soils, based on laboratory data, arises because in heterogeneous systems there can be more than one rate constant. Each rate constant has its own temperature dependence.

9-3.6 Soil Water Content

Water cannot only act as a solvent and transport agent for pesticides in soils, but it also can be a reaction medium for both biological and chemical processes. Furthermore, it is a reagent in hydrolytic reactions (Mabey & Mill, 1978).

Several studies (Walker, 1978; Kibler, 1979) have shown that degradation rates of many pesticides increase with increasing soil moisture to the

Table 9–2. The effect of sediment concentration on the hydrolysis of 1,4-DCB.

Sediment/water ratios	k_{obs} (min^{-1})	
	AR†	OK‡
g/g		
0.1	7.80×10^{-4}	5.91×10^{-4}
0.2	9.22×10^{-4}	7.17×10^{-4}
1.0	14.50×10^{-4}	16.72×10^{-4}
2.0	18.00×10^{-4}	16.50×10^{-4}

† Arkansas. ‡ Oklahoma.

point of maximum field capacity. In a study of methyl parathion, Mingelgrin et al. (1975) reported that as the soil moisture was reduced to 15% water content the disappearance rate constant increased and then decreased as the water content dropped below 9%. In a recent study by El-Amamy and Mill (1984), the hydrolysis rate constants of three organic compounds (ethyl acetate, cyclohexene oxide, and isopropyl bromide) in unsaturated clays (11% water content) were as much as a factor of 10 higher than the rate constants in pure water, presumably due to an enhanced acidity at the clay surface. Recently, Moftah and Wolfe (1988, unpublished data) observed a similar effect of solids on the hydrolysis of organic chemicals. Sediment/water ratios of 2:1 resulted in a threefold increase in the disappearance rate constant of 1,4-DCB when compared to the same system with a 1:10 ratio (Table 9–2). This suggests that sediment concentration and water content play an important role in the mechanism of hydrolysis in soils.

9–4 SUMMARY AND CONCLUSION

Until recently, the focus of studies of abiotic transformations of anthropogenic chemicals in natural waters, sediments, and soils has been directed to product formation. Because of recent efforts to model the transport and transformation of specific organic compounds in soils and sediments, there is an increased need for kinetic expressions that describe these processes. In general, these kinetic equations incorporate a distribution expression coupled with a second-order reaction. From a fate of pollutants perspective, transformations are for convenience divided into hydrolysis and redox processes. In this chapter, hydrolysis in saturated soils is examined. Disappearance kinetic expression are proposed that account for hydrolysis in both aqueous and solid phases. Observed rate enhancements and retardations are related to the pH of the system and the reaction pathway. The state-of-the-art of hydrolytic processes in heterolytic reaction media is assessed.

As it has been pointed out, pH can influence the degradation kinetics of pesticides in soils and sediments, but the details of the mechanisms involved are not fully understood, and more information is required before any general conclusions can be made. The experimental approach used by most workers of adjusting the pH of soils by the addition of acid or base

has been criticized because such treatment can cause changes in soil characteristics other than pH (Hamaker, 1972). Thus, the use of more representative model systems would be preferred. Better information could be obtained, for example, by adjusting the pH of field plots and using these soils for laboratory and field studies (Hurle & Walker, 1980).

Collection of data from different sites at different times of the year over sites with a large range of physical and chemical properties will enhance development of predictive equations for use in fate models.

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